HEUSE

# The Vapor Pressures of Aqueous Solutions of Electrolytes

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# THE VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF ELECTROLYTES

BY

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B. S. Hanover College, 1900
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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

EDWARD OTTO HEUSE

ENTITLED THE VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF ELECTROLYTES.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Doctor of Philosophy.

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This investigation was carried out at the suggestion and with the assistance of Professor E. W. Washburn.

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## I. PURPOSE AND OUTLINE OF THE INVESTIGATION.

The primary purpose of this investigation is the study of the condition of dissolved substances in aqueous solution, with especial reference to the question of the extent and nature of the union between solvent and solute in the solution. For such an investigation, there are theoretically available four principal methods of attack. These are the methods of freezing point lowering boiling point raising, osmotic pressure, and vapor pressure lowering.

The first two - the freezing point and the boiling point methods - have the disadvantage that it is necessary to change the temperature and the concentration of the solution simultaneously, while the method of osmotic pressure has only a limited applicability, because of the difficulty of preparing suitable semi-permeable membranes. The boiling point method also has the disadvantage that the boiling point changes quite considerably with changes in atmospheric pressure.

With the method of vapor pressure lowering, the concentration of the solution may be changed at will without changing the temperature, and it is also possible to make determinations for one concentration over a large range of temperature. Several methods for the measurement of vapor pressure of solutions have been proposed by various investigators,(1-13)and the study of one of these - the air-saturation, or dynamic method - was undertaken in this labratory several years ago, (14)and an apparatus developed which proved sufficiently accurate to

warrant further prosecution of the investigation by this method. The present undertaking is, therefore, really a continuation of the previous investigation with some modifications and improvements in the method and apparatus, that were suggested by the previous work, Using this improved apparatus, I have undertaken to measure the vapor pressure lowering produced by uni-univalent electrolytes in aqueous solution of moderate concentrations. For the purpose of securing a reference curve, some determinations were also made of the vapor pressure lowering produced by cane sugar.

## II. DESCRIPTION OF THE METHOD.

The essential features of the method can best be understood by a study of the diagrammatic sketch of the apparatus shown in Figure I. A current of air is first passed through the tube (T), containing soda-lime to remove carbon dioxide. It then passes through a pre-saturator ($P.S._1$) where it becomes supersaturated with water vapor, and then enters the first saturator ($S._1$) of the system, which contains pure water. From here the saturated air passes to the first drying apparatus, (or absorber) ($A._1$), where the water is all removed. It then passes directly to the second pre-saturator ($P.S._2$), containing water, and thence to the second saturator ($S._2$), which contains the solution under investigation. From here it passes through a second absorber ($A._2$), where the water is again all removed. The dry air then passes directly to the third saturator ($S._3$), also filled with water, and then thru the third absorber ($A._3$) , and so out of the system.

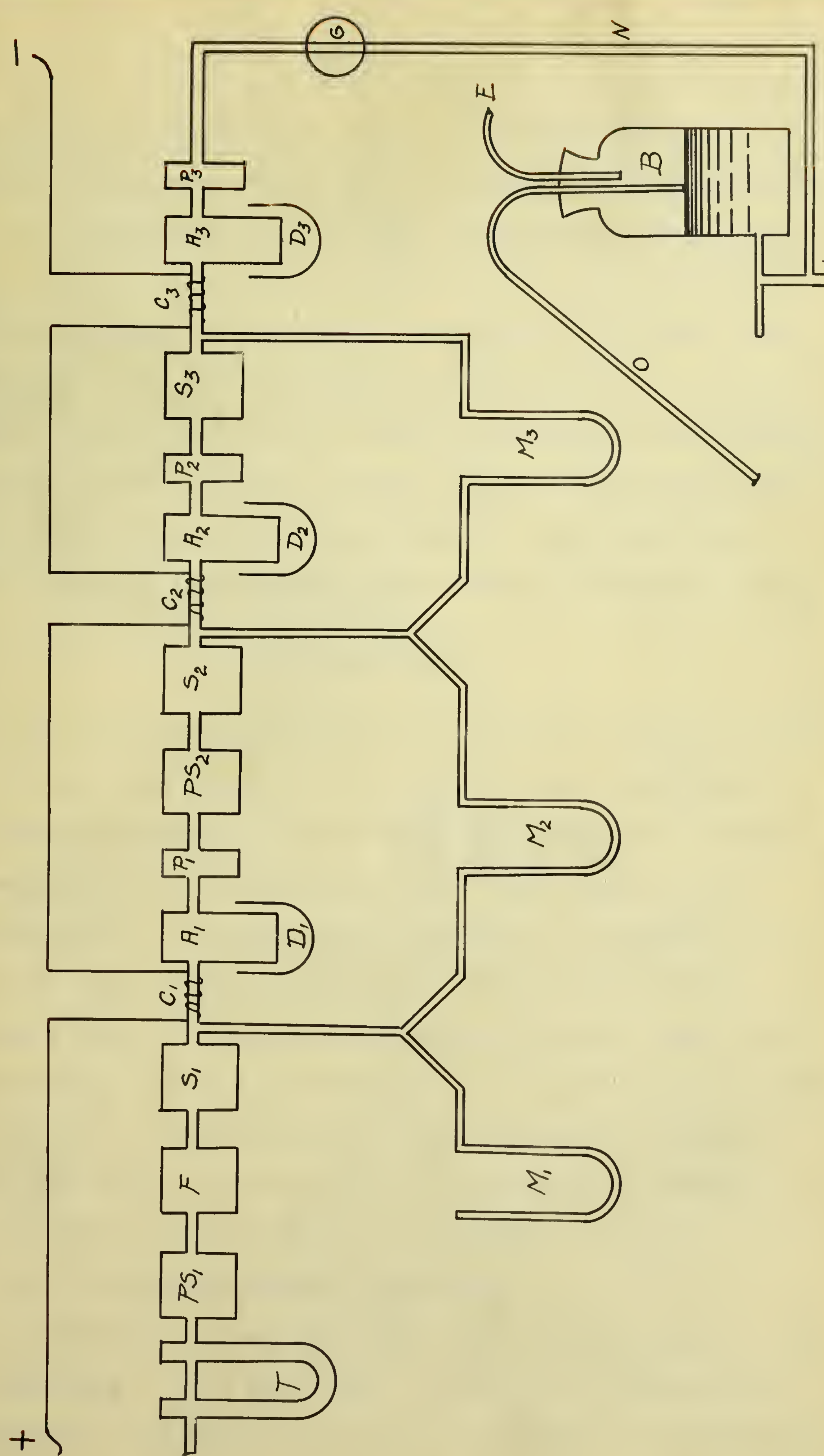

+
−
T
$PS_1$
F
$S_1$
$C_1$
$A_1$
$D_1$
$P_1$
$PS_2$
$S_2$
$C_2$
$A_2$
$D_2$
$P_2$
$S_3$
$C_3$
$A_3$
$D_3$
$P_3$
G
N
$M_1$
$M_2$
$M_3$
O
E
B
L

Figura 1

The pressure differences between the different parts of the apparatus, and between these and the atmosphere, are measured by means of the manometers, $M_1$, $M_2$, $M_3$, connected as indicated in the figure.

The difference in the gains in weight of the first and second absorbers, ( or the third and second absorbers), divided by the gain in weight of the first absorber, (or the third absorber), corrected for the pressure changes, gives at once the value of the relative vapor pressure lowering, without the necessity of knowing the volume of the air which was passed through the system.

## III. APPARATUS.

(A) The Pre-saturators- These consisted of 250 cc. flasks about half filled with water. To the tube by which the air enters the flask there is attached a cloth bag, which dips into the water. The positions of the pre-saturators ($PS_1$, $PS_2$, $PS_3$) in the system are indicated in Figure I. The purpose of the first pre-saturator is to supersaturate the air as it enters the system. This is accomplished by having the temperature of the flask about 30° C., by means of the hot plate (H). That the air really becomes supersaturated in the time required to go through this flask is evident from the deposit of moisture in the flask (F), which is submerged in the thermostat. The air thus enters the first water-saturator ($S_1$) in a supersaturated condition.

The second pre-saturator ($PS_2$), which also contains pure water, is submerged in the bath, and is thus at the temperature of the experiment. Its purpose is to bring the aqueous content of

the air approximately to the point of equilibrium before it enters the solution-saturator ($S_2$), and thus to diminish the change in concentration of the solution in this saturator.

No pre-saturator was used before the third saturator as it was desired to have the air enter this saturator perfectly dry. By so doing, a valuable check was secured on the result obtained from the first saturator, which the air entered in a supersaturated condition.

(B) The Saturators - These are indicated in the diagram as $S_1$, $S_2$, $S_3$, and are shown in a photograph on page 6. They were constructed of tubing about 12-15 mm. in diameter, except that the connecting tubes were about 7 mm. in diameter. The length of the saturators was about 40 cm., and the bulbs at the end, which were about 2.5 cm. in diameter, were for the purpose of breaking any films that might be formed, and thus to prevent the mechanical carrying over of water which would tend to cause an uneven distribution and erratic pressure differences. At first, ground glass stoppers were used in the saturators, but as these parts seemed more likely to crack, the later saturators were made without glass stoppers and were closed with rubber stoppers covered with tin foil; except that in the saturator containing the solution, the opening nearest to where the air entered was provided with a glass stop-cock into which were sealed platinum electrodes for the purpose of testing the conductance of the solution at different times during the run, to be sure that its concentration was not changing appreciably.

The saturators were rocked back and forth so that at the

end of each swing the one end of the saturator would be filled with the liquid, thus compelling the air to pass through the other end. The air entering at the center of the saturator, thus passed alternately through one or other of the ends. As there were four complete oscillations per minute, a large surface was constantly wet with fresh liquid. This movement together with the presence of a quartz bead in each of the tubes of the saturator, also insured thorough stirring of the liquid. The total length of the eight tubes of the saturator was over 300 cm., and it is probable that the air was saturated by the time it had gone half this distance.

(C) The Absorbers - These are indicated in the diagram at $A_1$, $A_2$, $A_3$, while a photograph of an absorber is shown on page 6 The length of the parallel tubes is about 14 cm., and thus the photograph is about one-tenth of the natural size. The air enters the absorber thru the flask, which is surrounded by ice and water in a Dewar tube, and most of the moisture is condensed here. The four parallel tubes contain concentrated sulphuric acid, and are about 12 mm. in diameter. The last two parallel tubes, which are of about the same diameter, but only about 9 cm. in length, contain phosphorus pentoxide and glass beads, (for keeping the phosphorus pentoxide loose).

The tube by which the air leaves the absorber, contains also some glass wool to prevent the mechanical carrying out of any of the pentoxide by the air current. These tubes are provided with stop cocks, which are kept closed except during a run. The tubes containing the sulphuric acid have enlargements along the bottom for the purpose of securing a larger volume of the acid.

As the flask of the absorber would hold about 30 cc. before the water reached the end of the inlet tube, a set of absorbers may be used for two runs before removing the water or renewing the sulphuric acid. The upright tube near the flask is closed by a solid ground glass stopper which is removed for cleaning and filling the apparatus. The openings in the stop cocks were the smallest places through which the air had to pass in going through the system, and these were, in most of the absorbers, about 4mm. in diameter and in no case less than 2mm.

(D) The Safety Tubes - These are shown at $P_1$, $P_2$, $P_3$, in Figure I. They were straight calcium chloride tubes and contained phosphorus pentoxide of the same quality as that in the absorbers, and also glass beads and glass wool. Their purpose was to prevent any moisture getting into the absorbers from the adjacent pre-saturator or saturator and in the case of $A_3$ to prevent any moisture entering from the aspirator bottle, tho in most cases this was further guarded against by the presence of the gas wash bottle (V), which contained concentrated sulphuric acid. Between runs, the safety tubes were either removed from the apparatus, or else themselves protected from the pre-saturators and saturators by means of screw clamps.

(E) The Heating Coils, $C_1$, $C_2$, $C_3$ - As the saturated air, in passing from a saturator to its absorber, had to pass, for a short distance through the air, and as the room was usually at a temperature below 25°, the part of the air channel thus exposed was covered with a coil of small wire, through which was passed a current of 3.5 -4 amperes, this amount having been found to give

sufficient warmth to prevent condensation at this point. An ammeter was connected in series with the coils, and thus it was only necessary to note the ammeter reading to be sure that the coils were working satisfactorily. The heating coils were covered with asbestos sheet to protect them.

(F) <u>The Frame, or Apparatus Support</u> - The saturators and absorbers and their connections, and also the Dewar tubes (shown at $D_1$, $D_2$, $D_3$,) - in fact all of the apparatus train shown in the Figure from F to $P_3$ inclusive, was fastened onto platforms as is shown in the photograph on page 10. Comparing the photograph with the diagrammatic sketch (Figure I), the bottom shelf contains the flask F ; the next higher shelf carries the first saturator ($S_1$); the next, or third, shelf the saturator $S_2$, and also the axle on which the whole frame rocks. The fourth shelf supports the third saturator ($S_3$), while the fifth acts as a support for the Dewar tubes, and also contains the second pre-saturator. The top shelf contains the absorbers and the safety tubes. When the frame is in position in the thermostat, all the shelves except the top one are submerged.

Running vertically, on the side where the axle protrudes, may be seen, near the farther edge of the frame, the tubes leading from the second saturator to its absorber, (the corresponding ones connecting the first and third saturators to their absorbers being on the other side of the frame). Coming up just past the axle, and fastened to it, are seen the glass parts of the three pressure tubes i.e. the tubes leading from the points where the air leaves the three saturators, to the manometers, the last part of this

connection being made with a good quality of thick walled rubber tubing, since the manometer must of course be stationary, while the glass tubes move with the frame.

By having all of these parts thus fastened to the one frame, no flexible joints are necessary, as the entire apparatus rocks together as one unit. The connections were thus in all cases, except those to the manometers, and to the air entrance and exit, made glass to glass and covered with heavy rubber tubing, wired on, and protected with a coating of a mixture of beeswax and rosin.

The frame was constructed of wood, and before being placed in the bath was entirely covered with hot parrafin which soaked into the wood. As is evident from the photograph the frame was a skeleton frame; i.e. it was sufficiently open so the water would have easy access to all parts of the immersed apparatus; the shelves were in fact each composed of three boards ( i,.e. two at the ends and a center board) each about seven eighths inch wide. The frame was placed in the thermostat, which will be described later, and the axle fastened by means of metal straps to wooden hubs, which were themselves fastened to the sides of the thermostat.

(G) <u>The Manometers</u> - These together with their connections are shown in Figure I at $M_1$, $M_2$, $M_3$. Manometer number one is connected with, and thus indicates the pressure difference between, the atmosphere and the first saturator: manometer number two is likewise used to find the pressure difference between the air as it leaves saturator one, and as it leaves saturator two: while the third manometer is used to find the pressure difference

between the air as it leaves saturator two and as it leaves saturator three. $K_1$-----$K_5$ are stop cocks by means of which the manometers were shut off from the rest of the apparatus, except when a pressure reading was being made.

The manometers themselves were of the open U type and contained water. The three were mounted on a meter stick which was securely fastened along the edge of a one inch oak board, sawed at such an angle (previously calculated and marked off) that 1 mm. on the scale was equivalent to a pressure of 0.005 mm. of mercury. This oak board with meter rule thus fastened to it, was mounted on the side of the thermostat as shown in Figure II MM'.

(H) The Aspirator System - The air was drawn through the apparatus by means of an aspirator pump, shown at L in the sketch (Figure I). This was attached to a 32 L aspirator bottle (B); which was provided with an overflow (O), the purpose of which was to maintain a constant level over the pump. The water entered the aspirator bottle from the tap by means of the tube E, and the rate of the air flow through the apparatus was controlled by means of the screw clamp (N), attached to the rubber tubing which connected the pump to the outlet of the aspirator bottle. The connection from the pump to the apparatus train was of glass with rubber joints, except for about 30 cm. of rubber tubing at the exit from the third absorber, this needing to be flexible because of the movement of the frame.

Before leaving Figure I, reference might also be made to the gas meter (G), which was used to measure the rate of flow of the air, tho in some of the work this was replaced merely by the

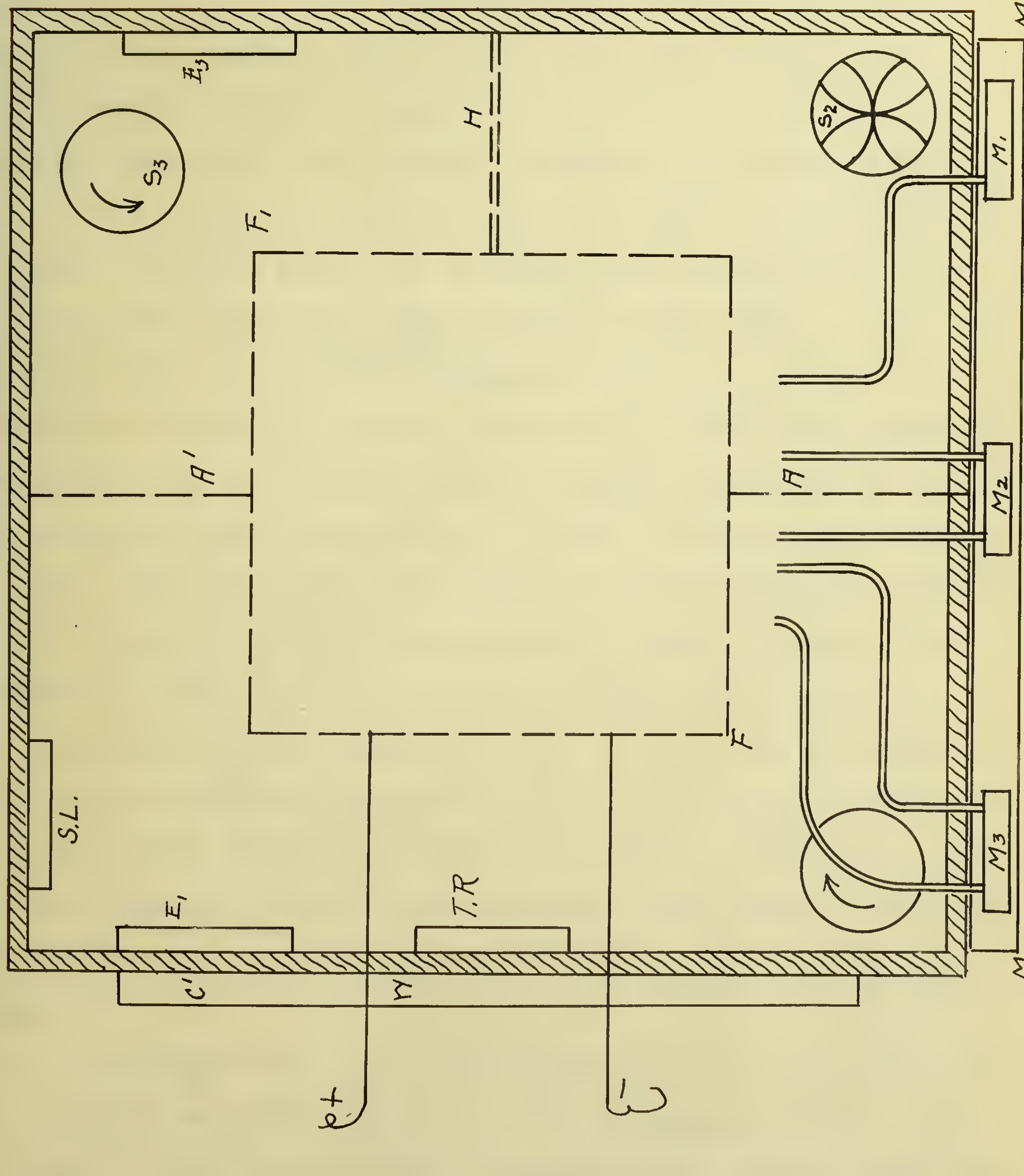



Figure 2.

gas wash bottle (V), where the rate of bubbling served as an approximate indication of the rate of flow.

(I) <u>The Thermostat</u> - This was a box three by three feet square, and three and one half feet deep. It was constructed of wood about two inches thick, and the inside was painted with several coats of bath tub enamel. It was provided with an overflow, and was filled, and emptied, by means of permanent siphons.

The apparatus contained in it, as also its distribution, is shown in plan in Figure II. The heavy line is the outline of the box itself. The dotted line shows the frame ($FF'$) in position, its axle ($AA'$), and the handle (H) by which it is rocked. SC is the steam coil by which the water is heated up to about the temperature desired; $C_1$, $C_2$, $C_3$, are the electric heaters by which the rest of the heating is done, and by means of which, along with the thermoregulator (TH) and a relay (not shown), the temperature is regulated during a run. $S_1$, $S_2$, $S_3$, are stirrers, $S_1$ and $S_3$ being of the Archimedes screw type, ($S_1$ sending the water down, and $S_3$ raising it), while $S_2$ is a fan stirrer. $M_1$, $M_2$, $M_3$, are the manometers, and W is the Wheatstone bridge for use in conductance measurements, as above stated. N and $N'$ represent the rubber connections leading from the pressure tubes to the manometers; and H and $H'$ indicate the wires carrying the current to the heating coils $C_1$, $C_2$, $C_3$, Figure I.

The power for rocking the frame, and also for operating the stirrers, was furnished by a $\frac{1}{4}$ HP. alternating current motor with 1100 R.P.M. This drove the stirrers at the rate of 400 R.P.M. and a worm gear was used for reducing the velocity to 4 R.P.M. for

the wheel rocking the platform.

(J) <u>The Thermo-regulator</u> - This was a combination of the one described by Regaud(15) and by Bousefield(16). It was filled with hydrogen gas, and an approximate mercury adjustment made when the room had been at just 25° an hour or two. For making final and exact adjustment, the regulator was mounted on a board; another board was fastened to the side of the thermostat, and provided with a screw bolt and nut. The board carrying the manometer was fastened to this board by the bolt and nut, which permitted a tilting of the regulator board at various angles. The setting used was such that the temperature at which the relay operated to shut off the heating coils $E_1$, $E_2$, $E_3$, Figure II, was found to be 24.995°.

The Beckmann thermometer which was used in making this temperature reading and which was used in the bath throughout the investigation was standardized by a comparison with a Standard Laboratory Thermometer. The regulator was found to operate i.e. to open and close the relay, with a change of temperature of .02° .

## IV. OUTLINE OF A TYPICAL RUN.

(A) The Saturators - Before these were used they were cleaned with a mixture of potassium dichromate and sulphuric acid, and carefully rinsed, the last rinsing being with distilled water. By means of the openings at the ends, all of the tubes except the last were about two fifths filled with water or the solution and a quartz bead placed in each tube. The last tube was left empty for the reason that in some of the runs there seemed to be a mechanical carrying over of water from this last tube into the pressure

tube (the tube leading from the saturator to the manometer), caused perhaps by the absence of a bulb between them. The total amount of liquid in each saturator was found to be about 170 cc. The saturators were fastened to the frame by means of wire, the tubes being thus supported at their ends and in the center. They were connected to the pressure tube, (which had a side tube leading to the absorber), by placing the ends of each in contact i.e. glass to glass, within a short piece of thick walled rubber tubing. This tubing was then fastened tightly at each end by copper wire and the whole then covered with the beeswax rosin mixture. As long as there was not a breakage, a saturator containing water very seldom needed to be removed from the frame, since if the supply of water became at all low in any of the tubes, more could be added by just removing the stopper of that part, and adding water by means of a pipette. The stoppers of these parts of course also had to be covered with the beeswax rosin mixture. The solution-saturator had to be removed whenever any change was made in the solution. It was first emptied and rinsed thoroughly with water, and then with some of the solution to be used before the solution itself was added. After the saturators were filled and connected in position, the frame could be placed in the thermostat, and left until a change of solution in the saturator, or a leak, necessitated its removal.

(B) The Absorbers - These also were cleaned with sulphuric acid and dichromate, rinsed with water, and then with alcohol and dried by use of dried compressed air. The sulphuric acid was then put into the absorber by introducing it into the upright tube, and was distributed through the four horizontal tubes by tilting

the absorber. These tubes were about two fifths filled with the acid, of which there was approximately 40 cc. The phosphorus pentoxide and the glass beads and glass wool were then introduced into the last two horizontal tubes of the absorber and the stop cocks lubricated with a very small quantity of vaseline, care being taken not to allow any of it to work out of the cock, where it might be wiped off in cleaning the absorber and thus change its weight. The absorber was prepared for weighing by cleaning the outside thoroughly and wiping it nearly dry with a damp cloth free from lint.

The absorbers were weighed on a large Ruprecht balance in a constant temperature room, the balance being sensitive to a tenth of a milligram with this load. The absorber to be used with the solution and which was by selection the heaviest of the set of three, was placed on the left pan of the balance, (whose zero point had been previously determined), and one of the absorbers to be used with a water saturator was placed on the right pan. Weights were then added to the right pan (and the rider adjustment made) until equilibrium was attained. After a few hours the weights were again adjusted. If, in the interval between the two weighings, the temperature of the balance case had changed more than a tenth of a degree, as indicated by a thermometer in the balance case, the absorbers were first opened for a moment to the air to secure pressure equalization, before the weights were readjusted. This procedure was continued at intervals of several hours until the re-adjustment required was not more than a few tenths of a milligram- often the last re-adjustment was not more

than one tenth of a milligram. The water absorber was then removed, the weights being checked with the records previously made as they were removed from the pan, and the weight of the solution absorber found. The other water absorber was then put on the right hand pan, and the difference between it and the solution-absorber determined in the same manner as above. As a check on the weight of the solution absorber it was usually weighed again after the removal of the second water absorber.

(C) Test for Leaks - Before each run the apparatus was tested for leaks. The thermostat was first filled full enough to submerge practically all parts of the apparatus except the absorbers i.e. water was let in to just below the top shelf of the frame, - the usual level being about half way between the top shelf and the one just below it. At each place where an absorber was connected in the run, there was placed a glass tube, each of these three tubes in turn being connected with the air line i.e. the channel by which the air went from the apparatus system to the aspirator pump. By means of a Y tube, connection was made to the compressed air supply and a bottle with an open arm mercury manometer was connected in series with the part of the apparatus being tested. When the pressure had reached a value equal to ten or fifteen times what would be experienced in a run, notice was taken of any escaping air bubbles, and also whether the manometer pressure stayedconstant for some little time. If leaks were found, they were repaired and that part of the apparatus again tested before proceeding with the run.

(D) Temperature - The extra water was then let out of the

tank by means of the overflow and several siphons, and the water of the bath brought to about 25°.by means of the steam coil indicated at SC in Figure II, which extended vertically through the water to within a short distance of the bottom of the bath. The last part of the heating, as also the regulating during the run, was done by means of the three electric heaters, $E_1$, $E_2$, $E_3$, Figure II, which were controlled by the thermoregulator and relay. In the Summer when the room temperature was sometimes above 25°, the water of the bath was kept from getting too warm, by having a stream of water running into the thermostat near the steam coil, the water from the tap being always below 25°. At times this supplemented by the use of a lump of ice hung over one corner of the thermostat near one of the stirrers, the rate of melting being of course controlled by the temperature, and thus the supply of cold water was regulated automatically.

(E) Miscellaneous - While the bath was coming to the proper temperature, the manometers were examined to see if any correction needed to be made for zero reading and to be sure that they were working properly. The aspirator system was also tested to be sure it was working satisfactorily, and the currents arranged for the operating of the relay and the air heaters, $C_1$, $C_2$, $C_3$, Figure I. During this time also the ice was prepared and placed in the Dewar tubes. It was found advantageous to use rather large lumps of ice as by so doing it was not necessary to add so much ice during the run. While ice was generally added to be sure of its lasting over night, there were usually some lumps of ice still found in the bottom of the Dewar tubes at the

end of a twenty-four hours run.

(F) Equilibrium Run - When the proper temperature had been attained by the bath, as shown by the Beckmann, and also by the action of the thermo-regulator, a preliminary or equilibrium run was made. For this purpose there were connected in place of the weighed absorbers two extra absorbers. A third absorber is obviously not needed in this run as the air can here be allowed to pass from the third saturator directly out of the apparatus system. The stop cocks of these were then opened and the air aspiration begun, and allowed to continue for about an hour. The purpose of this procedure is to bring all parts of the air channel into equilibrium with the moist air in the saturator.

(G) The Regular Run - At the end of the equilibrium run the air was dis-connected from the apparatus, the extra absorbers removed, and the three weighed absorbers put into their proper places and connected as before mentioned. Their stop cocks were then opened and the air stream again connected with the apparatus system, and the regular run was thus started. If the solution employed was that of an electrolyte, a measurement of its conductance was first made by stopping the frame in a certain marked position and taking a reading of the bridge. Just at the time of starting a run the barometer reading is taken. If no accidents occur, such as the slipping of belts, or breakiin an electric circuit, the chief part of the manipulation during the run is to keep the Dewar tubes supplied with ice, and to take readings of the barometer and manometers. These are usually taken about every three hours, although if

either of them is changing rapidly or erratically, more frequent measurements are taken. When the barometer shows any very large or sudden change, use is made of a barograph record in getting the mean value of the barometer pressure during the run. As the frame was kept in motion during the time of reading the manometer, the readings were fluctuating to a greater or less extent. Each manometer was therefore watched during several oscillations of the frame, and when its meniscus was at about the mean value, the stop cocks were closed and the reading taken. The different readings of any one manometer, at the different times during the run, very seldom differed very much - usually by not more than the experimental error of taking this reading.

With electrolytes, a bridge reading was usually taken at some time during the run, the apparatus being brought to a stop at exactly the same place as before. In no case, however, was there found to be any appreciable difference in the reading. Thus in one case the bridge reading at the beginning of the run was 93.0 and after the run had been going about eighteen hours the reading was 93.1 which with the apparatus used, was probably within the limits of observational error.

(H) Completion of Run - When the desired length of time had elapsed - usually twenty-four hours, tho one water run was continued for fifty hours - the air was disconnected from the apparatus train, and the stop cocks of the absorbers were closed, as were also the screw clamps connected with the pre-saturators. The absorbers were then removed from the frame, very carefully cleaned, and weighed, as described above. A sample set of weigh-

ings of the absorbers for a run might be of interest.

Weights before the run.

(1) Absorber 2 = Absorber 1 + 35.1289

(2) Absorber 2 = Absorber 3 + 35.7000

(3) Absorber 2 = 341.3595

Weights after the run.

(4) Absorber 2 = Absorber 1 + 34.8913

(5) Absorber 2 = Absorber 3 + 35.4611

(6) Absorber 2 = 352.7670

It is thus seen that the difference in gain of absorbers 2 and 1 during the run was 35.1289 − 34.8913 = 0.2376 g. while the difference in gain between absorber 2 and absorber 3 was 35.7000 − 34.4611 = 0.2389 g. The gain of absorber 2 i.e, the amount of water taken up from the air, after it became saturated over the solution, was obviously the difference between weights (3) and (6) i.e. 11.4075 g. This amount added to the difference in gain between absorbers 2 and 1 i.e. 11.4075 + 0.2336, or 11.6451 would then be the amount of water taken up by the first absorber, while 11,4075 + 0.2389 = 11.6464 g. was the amount taken up by the third absorber. If at all times during the run the total pressure had been the same in absorbers 1 and 3, i.e. if there were no fall in pressure through the system, the amounts of water taken up by the two absorbers should have been the same. Judged from this basis, it can be seen that there was not very much difference in the total pressure in the two saturators. This is also evident from the following list of pressures from this same run.

| Time | Manometer 1 - | Manometer 2 - | Manometer 3 |
|---|---|---|---|
| 2:30 P.M. | 75 | 13 | 9 |
| 5:00 P.M. | 75 | 13 | 9 |
| 8:00 P.M. | 79 | 13 | 11 |
| 7:30 A.M. | 81 | 15 | 28 |
| 10:30 A.M . | 77 | 21 | 26 |
| 2:30 P.M. | 78 | 23 | 27 |
| Mean | 78 | 18 | 18 |
| Equivalent in mm. of mercury | 0.39 | 0.09 | 0.09 |

This run, however, is not quite a typical one in that the reading of the first manometer, while quite constant, was rather large. This was due to the fact that the soda lime tube had not been freshly filled for this run. Manometer 3 shows a larger variation than was usually the case. In arriving at a mean value, account was taken of the time - thus the reading for the long interval over night should be given greater weight than the readings for the shorter intervals - the mean is, in short, a weighted time average.

## V. THE CALCULATION OF THE RELATIVE LOWERING.

As was shown in the previous investigation (14), the formula for the relative lowering, as measured by the method and apparatus above described, is as follows, where R equals the relative lowering.

$$R = \frac{Dm(B-P_1-p_o) - m_o\ Dp}{m_o(B-P_2) - Dm\ p_o}$$

The letters in this formula have the following significance:

Dm - difference in gain of the solution-absorber and the water-absorber during the run.

B - The corrected barometric pressure.

$P_1$ - The difference in the pressure between sat. 1 and the air.

$P_0$ - The vapor pressure of pure water at 25°.

$m_0$ - The amount of water taken up by the water-absorber.

Dp - Difference in pressure between the solution-saturator and the water-saturator.

$P_2$ - The difference in pressure between the second sat. and the air.

The value used for $p_0$ in calculating the results of the investigation, was 23.71 mm. as given by Krauskopf (11). (Since making the calculations of this investigation, there has appeared, in the paper by Derby and associates, (12) the value 23.76 mm. for 25° C. As this would, however, in no case in this investigation, make as much as 0.1 % difference in the results, these have not been re-calculated.)

As shown in the derivation of the above formula by Gordon, the only assumptions involved are the perfect gas laws for vapors.

<u>Example of a Calculation</u> - The following shows a substitution in the above formula, the data being those for saturators 1 and 2 in run 12, Table II. The details of the weights and pressures for this run are given on pages 22 and 23.

$$R = \frac{0.2376(747.14-0.39-23.71) - 11.6451x.09}{11.6451(747.14-0.48) - .2376x23.71} = \frac{1171.796-1.048}{8695.0-5.6} = .0.01965.$$

## VI. THE EXPERIMENTAL DATA.

TABLE I. - Results with Water in All Three Saturators.

| Run No. | Saturators used in calculation | $m_o$ | Dm | Barom. | *$P_1$ | $P_2$ | $P_3$ | 100 R** |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 & 2 | 18.2417 | .0033 | 743.00 | 0.18 | 0.33 | 0.50. | .0027 |
| 1 | 2 & 3 | 18.2435 | .0051 | | | | | .0041 |
| 2 | 1 & 2 | 14.9149 | .0031 | 734.20 | 0.10 | 0.21 | 0.33 | .0051 |
| 2 | 2 & 3 | 14.9147 | .0029 | | | | | .0025 |
| | | | | | Mean Value | | | .0036 |

* The pressures here given are mean values (weighted-time-averages) and are expressed in millimeters of mercury.

** R - relative vapor pressure lowering.

The value of the relative lowering should, of course, be zero for the above runs. The values actually obtained are very small, as is especially noticeable when compared with the results gotten with the solutioms. The smallest value obtained in any of these was with half normal potassium chloride and the mean value from the water runs is only about ¼ of 1 % of that value, while it is less than 1/10 of 1 % of the largest value obtained - the one with normal lithium chloride.

There should be no dddfference in the value derived by use of saturator one, where the air enters supersaturated, and saturator three where it enters perfectly dry. As the higher value above in one run was gotten by use of saturator one and in the other by use of saturator three; and as the value given by satu-

rator one in either run is just about the same as that given by saturator three in the other run, it may be concluded that there is no appreciable constant difference, and thus no appreciable constant error, due to the apparatus or procedure.

TABLE II. Results with Solutions of Cane Sugar.*

| Run No. | Saturators used in calculation | $m_o$ | Dm | Barom. | $P_1$ | $P_2$ | $P_3$ | 100 R. |
|---|---|---|---|---|---|---|---|---|
| 11 | 1 & 2 | 11.7458 | .2401 | 749.01 | .24 | .29 | .31 | 1.974 |
| 11 | 2 & 3 | 11.7432 | .2375 | | | | | 1.957 |
| 12 | 1 & 2 | 11.6451 | .2376 | 747.14 | .39 | .48 | .57 | 1.965 |
| 12 | 2 & 3 | 11.6464 | .2389 | | | | | 1.975 |
| 13 | 1 & 2 | 4.8408 | .0996 | 740.56 | .09 | .13 | | 1.987 |

* All solutions were weight normal.

The following were the polariscope readings for the above solutions:

| For the solution used in | Before the run. | After the run. |
|---|---|---|
| Run 11 | $356.25^\circ$ | $356.00^\circ$ |
| Run 12 | $355.61^\circ$ | $355.58^\circ$ |

It is thus seen that there was practically no inversion in either case during the course of the run. The first sugar solutions that were used gave considerable trouble in this respect, due to the growth of fungus. This was remedied by adding to the later solutions, at the time they were prepared, sufficient mercuric chloride to constitute about 1/10 of 1 %. As this amounted to considerably less than 0.01 mole, no account of it was taken in the calculations.

TABLE III. Results with Solutions of Potassium Chloride.

| Run No. | Conc.** by Wt. | Sats. used in calc. | $m_0$ | Dm | Barom. | $P_1$ | $P_2$ | $P_3$ | 100 R. |
|---|---|---|---|---|---|---|---|---|---|
| 21 | 1.0296 | 1 & 2 | 10.5637 | .3488 | 739.60 | .21 | .50 | 1.77 | 3.161 |
| 21 | | 2 & 3 | 10.5789 | .3640 | | | | | 3.168 |
| 22* | | 1 & 2 | 7.9402 | .2581 | 739.4 | .16 | .27 | | 3.135 |
| 22 | .5073 | 1 & 2 | 12.3251 | .1777 | 750.8 | .07 | .18 | .30 | 1.388 |
| 23 | | 2 & 3 | 12.3280 | .1806 | | | | | 1.378 |
| 24* | | 1 & 2 | 6.0067 | .0863 | 740.38 | .30 | .48 | .95 | 1.373 |
| 25* | | 1 & 2 | 7.0076 | .1007 | 744.40 | .17 | .35 | | 1.368 |

** i.e. moles of salt per 1000 grams of water.

* In runs 22, 24 and 25 the data are given for only one pair of saturators, the results for the other pair, in each of these cases, being so far different from those here given , as to indicate an accident of some sort during the run.

TABLE IV. Results with Solutions of Lithium Chloride.

| Run No. | Conc.* by Wt. | Sats. used in calc. | $m_o$ | Dm | Barom. | $P_1$ | $P_2$ | $P_3$ | 100 R. |
|---|---|---|---|---|---|---|---|---|---|
| 31 | 1.020 | 1 & 2 | 3.6883 | .1659 | 753.26 | 0.15 | .24 | .30 | 4.3514 |
| 31 | | 2 & 3 | 3.6860 | .1636 | | | | | 4.2993 |
| 32 | 0.502 | 1 & 2 | 4.4714 | .0847 | 740.56 | .105 | .21 | .24 | 1.822 |
| 32 | | 2 & 3 | 4.4706 | .0839 | | | | | 1.813 |

* i.e. moles of salt per 1000 grams of water.

## VII. DISCUSSION OF RESULTS.

(A) - Raoult's Law - According to Raoult's law of vapor pressure lowering, the relative lowering of the vapor pressure of a solvent caused by dissolving a solute in it, is equal to the mole fraction of the solute in the resulting solution. (22). Expressed mathematically, this might be stated thus:

$$\frac{p_0 - p}{p_0} = \frac{n_1}{n + n_1} = x_1 *$$

In this formula the letters have the following significance:

$p_0$ - The vapor pressure of the pure solvent.

p - The vapor pressure of the solvent from the solution.

$n_1$ - The number of moles of the solute in the solution.

n - The number of moles of the solvent in the solution.

$x_1$ - The mole fraction of the solute in the resulting solution.

* - This equation is based on the assumption that the thermodynamic environment of the solution remains constant when the mole fraction of the solvent is changed.

From the above formula it may be seen that the curve for $x_1$ - R, i.e. the curve obtained by plotting values of $x_1$ as abscissas, and values of R as ordinates, would be a straight line with a slope of 45$^\circ$, as shown by the heavier line in Fig. III.

(B) Aqueous Solutions of Sucrose - Owing to the increased accuracy obtained with this method for measuring vapor pressure lowering, there are no vapor pressure data by other

investigators with which those obtained by this investigation could be fairly compared. There exist however some very accurate determinations of the osmotic pressures of cane sugar solutions at 25° (17) and a comparison of the results obtained in this investigation with these osmotic pressure values can be secured in the case of cane sugar solutions. For this purpose the relative lowering of weight molal cane sugar solutions was determined with the results already given in Table V. In order to compare these results with Morse's osmotic pressure values, the osmotic pressures were calculated by means of the purely thermodynamic (18) formula:

$$\Pi = \frac{R\,T}{V_o}\left[\frac{p_o - p}{p_o} + \frac{1}{2}\left(\frac{p_o - p}{p_o}\right)^2 + \frac{1}{3}\left(\frac{p_o - p}{p_o}\right)^3 + \cdots\right]$$

where the letters have the following significance:

$\Pi$ - The osmotic pressure.

R - The gas constant i.e. 0.08207 liter-atmospheres.

T - The absolute temperature of the experiment, in this case 298°.

$V_o$ - The molecular volume of the pure solvent, at the temperature T - In this case this is equal to 18 x 1.0002938 cc.

The osmotic pressures thus calculated are shown in column 5 of Table V and in the next column are the directly measured values obtained by Morse. It is evident that those calculated from the vapor pressure lowering are in perfect agreement with the directly measured ones. This agreement is a valuable confirmation of the vapor pressure method employed in this investigation. In Figure III, the point in the red circle *

TABLE V. <u>The Results with Cane Sugar.</u>

| Moles of sugar per 1000 g. of water | Mole fraction if not hydrated x 100 | Mole fraction if hexahydrate x 100 | 100 R. | Osmotic Pressure Calculated (17) | Osmotic Pressure observed (18) |
|---|---|---|---|---|---|
| 1 | 1.769 | 1.979 | 1.974 | 27.01 | 27.030 |
| 1 | 1.769 | 1.979 | 1.957 | 26.77 | |
| 1 | 1.769 | 1.979 | 1.967 | 26.88 | |
| 1 | 1.769 | 1.979 | 1.975 | 27.02 | 27.076 |
| 1 | 1.769 | 1.979 | 1.987 | 27.19 | |
| | | | Mean | 27.0 | 27.05 |
| | | Average Deviation | | 0.14 | 0.03 |

represents the position of the mean value of the vapor pressure lowering. It evidently shows considerable variation from the theoretical curve. If, however, the assumption be made that the sugar exists in the solution as a hexahydrate the mean vapor pressure lowering gives the position in the pink circle *, which is evidently in very good agreement with the theoretical curve, which is a further piece of evidence indicating that sugar is probably hydrated in solution to this extent. The fact that this is the same hydrate that exists in solution at $0^\circ$ C (27) would seem to indicate that the hydration is a comparatively stable one within the temperature range $6^\circ$ to $25^\circ$.

* The two mole fractions are calculated by means of the two equations:

$$\text{(a)} \quad x = \frac{1000}{18} \div \left(\frac{1000}{18} + N_1\right)$$

$$\text{(b)} \quad x = \left(\frac{1000}{18} - W N_1\right) \div \left(\frac{1000}{18} - W N_1 + N_1\right)$$

In both of these x represents the mole fraction of the water in a solution containing $N_1$ moles of sugar per 1000 grams of water. In equation (b) W is the number of water molecules which unite with one molecule of sugar, hence the free water is $\frac{1000}{18} - W N_1$.

(C) <u>Aqueous Solutions of Electrolytes.</u> - In order to calculate the mole fraction, when the solute was an electrolyte, it was first necessary to know its degree of dissociation in the solution under investigation. For calculating this use was made of the expression : $\gamma = \frac{\Lambda}{\Lambda_0} \frac{\eta}{\eta_0}$ the use of which for this purpose has been discussed by Washburn (23). No data for these

quantities at $25^{o}$ being available, use was made of the data for $18^{o}$ (20, 21).

The data for potassium chloride are given in Table VI. The value of the equivalent conductance ($\Lambda$) for each concentration used is given in column 5 of this table, while the corresponding values of the relative viscosity ($\frac{\eta}{\eta_0}$) are found in column 6, and the resulting values for the degree of dissociation are in column 7. For calculating the mole fraction of the solute, the following expression is given by Washburn and Mac Innes: (24) $x_1 = \frac{n\ (1+\gamma)}{\frac{1000}{18} + n\ (1+\gamma)}$

The values of 100 $x_1$, derived by use of this formula, are given in the last column of Table VI; and the values of $x_1$ as abscissas with the corresponding values of R as ordinates are plotted in Figure III.

From the table, and also from the curve for this salt, it may be seen that for the normal solutions the values of R are within about 1% of the values for $x_1$, which might be taken as a basis for the conclusion that at this concentration there is no union between solvent and solute. It is known however from other work (25) that the ions of potassium chloride are hydrated.

It might also be concluded from the closeness of agreement between the values for $x_1$ and R that the ions have exactly the same effect on the relative lowering (and so on the other colligative properties, since these are all necessarily connected according to the principles of thermo-dynamics (26) ) as do the undissociated molecules, and that both behave as normal solutes. If this were true it would constitute a real exception to the

TABLE VI. Results with Potassium Chloride.

| Moles of salt per liter of solution | 100 R. | Density of solution (19) | Moles of salt per 1000 g. of water | $\Lambda$ at 18° (20) | $\eta/\eta_0$ at 18° (21) | $\frac{\Lambda}{\Lambda_0}\cdot\frac{\eta}{\eta_0}$ at 18° | 100 $x_1$ |
|---|---|---|---|---|---|---|---|
| 1.0 | 3.135 | 1.0458 | 1.0296 | 98.27 | 0.9820 | .7417 | 3.130 |
| | 3.161 | | | | | | |
| | 3.168 | | | | | | |
| 0.5 | 1.388 | 1.0229 | 0.5073 | 102.41 | 0.9897 | .7790 | 1.599 |
| | 1.378 | | | | | | |
| | 1.373 | | | | | | |
| | 1.368 | | | | | | |
| 0.0 | | | | 130.1 | | | |

second law of Thermodynamics, since it would require that the mass action law hold for this solution, which is known not to be the case.

The values obtained with the half normal solution evidently deviate quite considerably from the theoretical curve, a behavior which is quite different from that found by Mac Innes (24) for potassium chloride solutions at $0^{\circ}$. This might possibly be ascribed to error of observation were it not for the fact that the four points obtained agree very closely with one another. In order to be certain on this point it will be necessary to make some determinations at about 0.75 normal. It is my intention to do this in the near future.

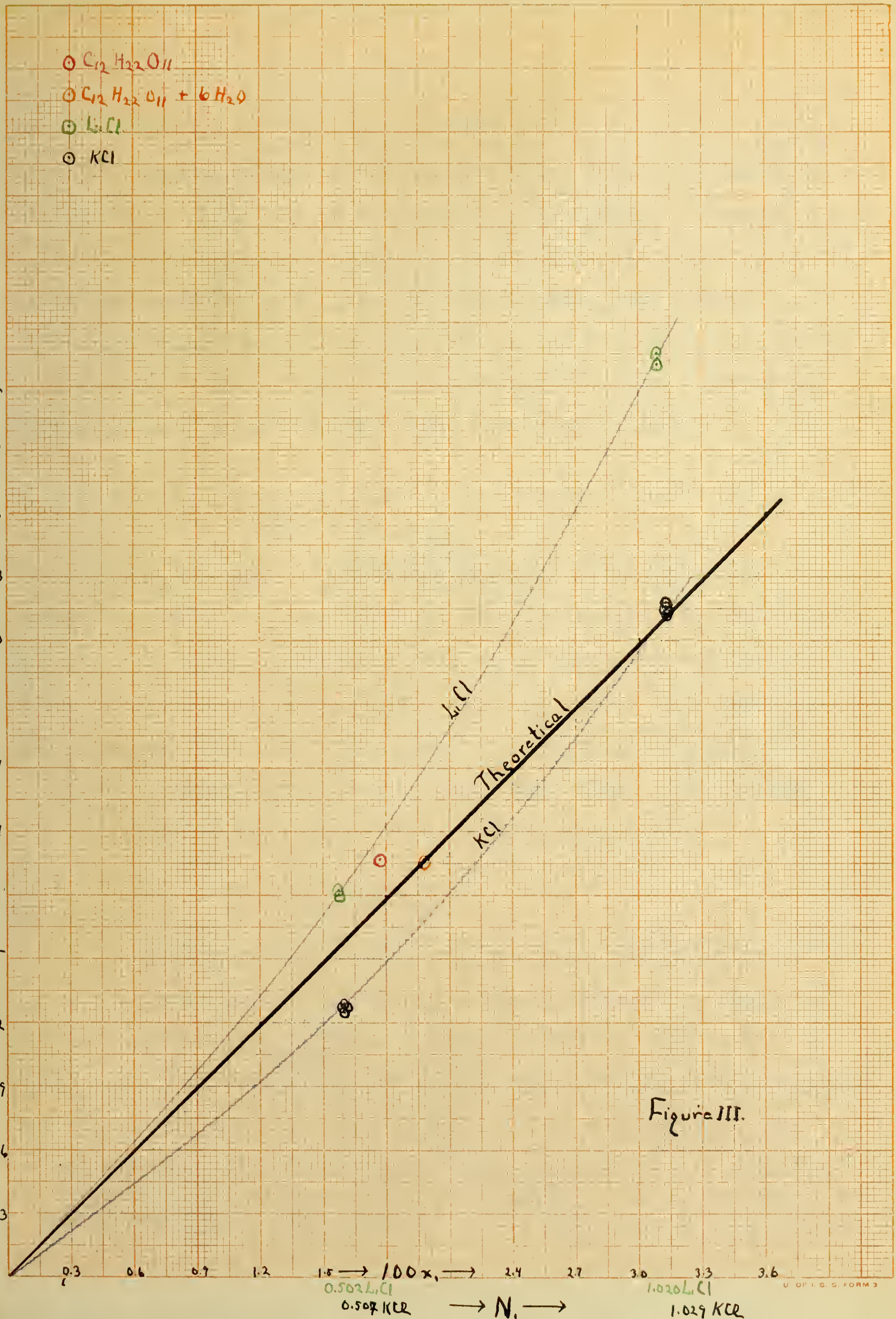
In the case of lithium chloride the degree of dissociation, and the mole fraction of the solute, for the different concentrations used, were calculated in the same manner as in the case of potassium chloride.

The values of the relative vapor pressure lowering given in column 2, of Table VII, are here again as in the case of sugar seen to be considerably larger than the corresponding values for the mole fraction of the solute (100 $x_1$) which are given in the last column of the table. It can also be seen from the graph (Figure III - page 38) that the curve for this salt deviates considerably from the theoretical curve.

If this salt were hydrated, the effect on its mole fraction would be the same as was found to occur in the sugar solution i.e. the value for the mole fraction would be increased, inasmuch as the number of moles of water which act as solvent

TABLE VII. Results with Lithium Chloride.

| Moles of salt per liter of solution | 100 R. | Density of solution (19) | Moles of salt per 1000 g. of water | $\eta/\eta_0$ at 18° | $\Lambda$ at 18° | $\frac{\Lambda}{\Lambda_0}\cdot\frac{\eta}{\eta_0}$ at 18° | 100 $x_1$ |
|---|---|---|---|---|---|---|---|
| 1.0 | 4.351 | 1.0228 | 1.0201 | 1.1498 | 63.36 | .73677 | 3.090 |
| | 4.299 | | | | | | |
| 0.5 | 1.813 | 1.0173 | 0.502 | 1.075 | 70.71 | .76874 | 1.573 |
| | 1.822 | | | | | | |
| 0.0 | | | | | 98.88 | | |



$C_{12}H_{22}O_{11}$
$C_{12}H_{22}O_{11} + 6H_2O$
LiCl
KCl
4.2
3.9
3.6
3.3
3.0
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
100R
LiCl
Theoretical
KCl
0.3
0.6
0.9
1.2
1.5
100x,
2.4
2.7
3.0
3.3
3.6
0.502 LiCl
0.507 KCl
N,
1.020 LiCl
1.029 KCl
Figure III.

would be decreased. Thus the denominator in the fraction $\frac{n_1}{n_1+n}$ would be decreased due to the smaller value for n; and since the value for $n_1$ would not be affected by this change, the value of the fraction would become larger. It can be seen from Figure III that the deviation which the lithium chloride curve shows from the theoretical curve is a deviation in the direction of a larger value of $x_1$. Thus it may be concluded that lithium chloride is hydrated when in solution. With the use of the formula

$$x_1 = \frac{n_1 (1 + \gamma)}{n_1 (1 + \gamma) + \frac{1000}{18} - h\, n_1}$$

calculation was made to ascertain how many moles of water (h) would be needed to bring the mole fraction of the lithium chloride in the half normal solution to the value corresponding to this same value of R on the potassium chloride curve, The value so obtained was about 12, which leads to the conclusion that the degree of hydration of lithium chloride at this concentration is twelve moles more than that of potassium chloride.

## VIII. SUMMARY.

An apparatus and procedure are described by which it is possible to determine the relative vapor pressure lowering of a normal salt solution with an accuracy of 0.25 %, and that of a half normal salt solution with an accuracy of 0.50 %. The accuracy of the method is also shown by the results with water in all three saturators, the mean value thus obtained for the relative vapor pressure lowering being 3.6 x $10^{-5}$ mm.

The method is, in brief, the saturating of a current of air by causing it to pass through a saturator containing water and also through one containing a solution, removing the water taken up in each case, and making a comparison between the mass of water taken up by the air in passing through the water saturator and the difference between this mass of water and that taken up in passing through the solution saturator.

The method is such that practically two determinations are obtained from each run, the one by use of a water saturator, which the air enters supersaturated, and the other by use of a water saturator which the air enters perfectly dry. These two determinations thus serve as a check on each other. The method is also such that the results would not be perceptibly influenced by a slight irregularity in temperature.

The apparatus is so constructed that the total pressure fall throughout the entire system is very small, usually being less than 0.5 mm. of mercury.

By the method here described a check has been secured with the osmotic pressure of Morse, with which the results of this investigation are in practically perfect agreement.

Cane sugar is shown to exist in aqueous solution at 25° C as the hexahydrate. As this is the same form in which it exists in aqueous solution at 0°, these results show something of the degree of stability of this hydrate over this temperature range.

The results with lithium chloride agree well with the results obtained by Mac Innes on the freezing point lowering caused by this salt. This is also true of the normal potassium

chloride solution. The half normal solution shows considerable deviation, which may be due to experimental error. It is planned to investigate this matter further, by more determinations both at this concentration and at 0.75 normal.

Lithium chloride in aqueous solution is probably hydrated to quite a large extent, both at normal and half normal concentrations. Potassium chloride in normal solution seems to agree excellently with the action of a normal solute; this is probably due to a compensation of two opposite influences.

## REFERENCES


(1) Regnault, Ann. de Ch. etde Phys. (3) 15, 158 (1845)

(2) Tamman, Wied. Ann. 33, 322 (1888)

(3) Walker, Zeit. Phys. Chem. 2, 602 (1888)

(4) Ostwald, Phys. Chem. Measurements, Walker's translation, 1894,188

(5) Dieterici, Wied. Ann. 62, 616 (1897)

(6) Perman, Proc. Royal Soc. 72, 72 (1903)

(7) Carveth & Fowler, J. Phys. Chem. 4, 313 (1904)

(8) Berkeley & Hartley, Nature, 1905, 222.

(9) Kahlenberg, Science 22, July 1905.

(10) Berkely & Hartley, Proc. Royal Soc. 77, 156 (1906)

(11) Krauskopf, J.Phys. Chem. 14, 489.

(12) Lincoln & Klein, J. Phys. Chem. 1907, 318.

(13) Derby, Daniels, Gutsche, J.Am. Chem. Soc. 36, 793 (1914)

(14) H. B. Gordon, Thesis, Illinois, 1912.

(15) Regand & Fouilland, Zents. (2) 80 , 1789.

(16) Bousfield, Chem. News 105, 13.

(17) Washburn, J. Am. Chem. Soc. 32, 497 (1910)

(18) Morse & Associates, Am. Chem. 45, 599 (1911)

(19) Landolt - Bornstein , Tables 4th edition.

(20) Gruneisen, Wiss. Abh. d. Phys. - Tech. Reichsanstalt 3, 210, (1900)

(21) Kohlrausch & Maltby, Ibid4, 239 (1905)

(22) Washburn, J.Am. Chem. Soc. 32, 665 (1910)

(23) J. Am. Chem. Soc. 33, 1461 (1911)

(24) Mac Innes, J. Am. Chem. Soc. 33, 1702 (1911)

(25) Washburn, Technology Quarterly & J. Am. Chem. Soc. 31, 322 (1909)

(26) Washburn, J. Am. Chem. Soc. 32, 496 (1911)

(27) Introd. to the Prin. of Phys. Chem. (Washburn) p. 150 Fig. 22.

Biographical.

The writer received his early education in the schools of Madison, Ind. In 1900 he graduated from Hanover College with the degree of Bachelor of Science (cum laude) and in 1906 he received the honorary degree of Master of Arts from the same institution. In 1907 he received the degree of Master of Science in Chemistry from the University of Illinois, his master's thesis having been published, under co-authorship with William M. Dehn in J. Am. Chem. Soc. 29, 1137 (1907) under the title - " The Decomposition of Hydrated Ammonium Salts."

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